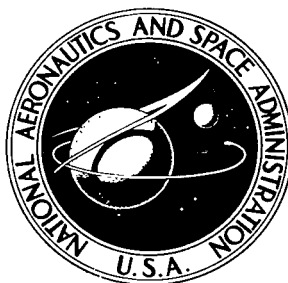


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RADIATION-INDUCED PREPARATION OF ANTIMONY FROM SOLUTIONS OF ANTIMONY (III) CHLORIDE IN ORGANIC LIQUIDS

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RADIATION-INDUCED PREPARATION OF ANTIMONY FROM SOLUTIONS OF ANTIMONY (III) CHLORIDE IN ORGANIC LIQUIDS

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SUMMARY

The yield of antimony metal (Sb) from the irradiation with 2-MeV electrons of antimony (III) chloride solutions in a variety of dry organic liquids is presented. These liquids include methanol, 1-butanol, 2-propanol, 2-methyl-2-propanol, glycerol, 3-heptanone, tetrahydrofuran, acetic acid, oleic acid, amyl acetate, dibutyl phthalate, toluene, ethylbenzene, and quinoline. The antimony is deposited as a reactive fine powder sensitive to atmospheric oxidation. Vacuum-dried powders produced from the less polar solvents were most reactive, and often pyrophoric.

The yield $n \cdot G(\text{Sb})$ (atoms of Sb per 100 eV multiplied by the valence change $n = 3$) ranged from 0 to 3.71; the greatest yield and the highest purity (99.9+ percent Sb) were obtained from primary alcohols. Secondary alcohols and cyclic ethers gave lower yields of less pure Sb, while the nonpolar liquids (aromatic hydrocarbons) resulted in even lower yields and Sb of poor quality. The contaminants consisted of carbonaceous residues derived from adsorbed organic substances. An important criterion for high antimony yields in organic liquids is the presence of hydrogen atoms on the functional group carbon atom. In addition, yield is increased by increasing the antimony (III) chloride concentration.

The application of dry organic systems to the production of metals in general is briefly discussed.

INTRODUCTION

Much of the work in radiation chemistry has been concerned with the pulse radiolysis of aqueous systems. This technique coupled with high-speed spectroscopy has not only helped investigators to identify short-lived species formed by ionizing radiation but

also has enabled the course of fast reactions to be observed. An important finding of this work is that the solvated electron, in this case the hydrated electron e_{aq}^- , is a major reducing species in water (ref. 1). The solvated electron has also been observed by optical absorption spectroscopy during the pulse radiolysis of organic liquids such as aliphatic alcohols, amines, and some ethers (ref. 2). The high reduction potential of the solvated electron for example ($E^0 = 2.67$ V for the hydrated electron) (ref. 3), and its high reactivity with many metal ions and metal ion complexes (ref. 4) suggest the application of radiation chemistry to inorganic synthesis on a macroscale, especially for the preparation of metal powders from metal salt solutions. It has already been shown that red colloidal gold appears on repeated pulsing of monovalent gold solutions containing methanol (ref. 5). The deposition of platinum (ref. 6), gold (ref. 7), and mercury (ref. 8) on gamma radiolysis of aqueous solutions has also been reported.

With this background in mind, we have been exploring the use of continuous-high-flux and high-energy electrons from a linear accelerator to prepare macroquantities of pure powdered metals from their salt solutions. Our interest in the radiological preparation of metals stems from the idea that high-purity finely divided metal powders can be produced by this method. Relatively low temperatures and simple systems may be used to minimize impurities due to reaction of the metal powder with the environment. Because the use of radiation chemistry for the production of metals is new and has received little attention in the literature, our present work, out of necessity, is exploratory in nature. The emphasis of our work, therefore, is to find out which metals will deposit from specified systems and also to study the effect of various systems and parameters on the yield, physical condition, and purity of the metals produced.

Our earlier reports (refs. 9 to 12) describe the deposition of metals from aqueous solution. Typically, a dilute aqueous solution (about 0.1 molar) of a metal salt (generally the sulfate, acetate, or chloride) containing a readily oxidizable organic compound (1 molar primary or secondary alcohol) was irradiated with 2-MeV electrons at 20 microamperes for a total dose of 0.1 to 0.2 coulomb. Radiation causes the metal to precipitate. The action of ionizing radiation on water produces hydrated electrons (e_{aq}^-) plus hydrogen atoms ($H\cdot$), hydroxyl radicals ($OH\cdot$), and hydronium ions (H_3O^+) (refs. 1 and 13). In the presence of certain organic reducing agents, the oxidizing OH radicals are scavenged. The solution thus becomes a source of reducing hydrated electrons and hydrogen atoms; these reducing species then react with the metal ion in solution to form the free metal. In aqueous copper (II) systems the primary alcohol, methanol, was effective as a scavenger for OH radicals (ref. 9). However, for the deposition of nickel, best results were obtained in basic ammoniacal solution, because the freshly produced nickel metal reacts with acids. Our most recent report (ref. 12) presents the yield of eleven metals, copper, zinc, cadmium, thallium, tin, lead, antimony, iron, cobalt,

nickel, and palladium, prepared from aqueous systems. The yields expressed as $n \cdot G(M)$ (where n is the valence change and $G(M)$ is the number of metal atoms produced per 100 eV) ranged from 0.001 for iron to 4.7 for palladium.

Aqueous systems, however, are limited to the preparation of the less electropositive metals, those which do not reduce water. Thus, in anticipation of making the more active metals, our present interest is in the use of water-free organic liquid systems. It is hoped that, in some cases, certain organic systems would afford higher product yields than were obtained in water solution. This report is concerned with an evaluation of common organic liquids for the preparation of antimony metal (Sb) from solutions of antimony (III) chloride ($SbCl_3$) in these liquids. The antimony system was selected because of the solubility of antimony (III) chloride in many organic liquids and because of the relative inactivity of finely divided antimony powder, which minimizes handling problems. The results of this study should aid in the selection of organic systems for the radiation-induced preparation of metals in general.

EXPERIMENTAL

Our selection of organic liquids (table I) gave a wide variety of functional groups. These liquids were either reagent, certified A.C.S., or C.P. grade except for U.S.P. glycerol, U.S.P. oleic acid, and practical 3-heptanone. Prior to use, all of the organic liquids were dried over anhydrous calcium sulfate for several days. The $SbCl_3$, certified A.C.S. grade, was used without further purification. In certain aspects of radiation chemistry such as pulse radiolysis, where very small chemical changes are observed, the need for ultra-high-purity starting materials is apparent. However, because of high radiation doses and the gram quantity of antimony produced in our experiments, the employment of elaborate methods to prepare these high-purity starting materials is unnecessary.

The reaction vessel and general procedure are described in earlier reports (refs. 9 and 14). Because of their hygroscopic nature, the $SbCl_3$ solutions were prepared in a stoppered flask immediately before use. In most cases the solutions were 0.25 molar in $SbCl_3$; however, in tetrahydrofuran and methanol other concentrations were used. The time involved in pouring the solution into the reaction vessel and closing the vessel to the atmosphere was kept to a minimum. The solution was agitated during the irradiation by passing helium through a glass frit at the base of the vessel. The contents of the vessel were kept below 30° C during this time by immersing the vessel in a water bath.

The electron beam was supplied by a linear accelerator. An arbitrary choice of 2-MeV electrons for all irradiations proved to be convenient for ease of using the ac-

celerator and at the same time affording sufficient penetration of the beam (1 cm) into the reaction medium. The diameter of the beam was about 4 centimeters. A beam current of 20 microamperes for a dose of about 0.20 coulomb (read on a beam current integrator) was selected because of practical considerations such as heat generation, irradiation time, and quantity of antimony produced.

After irradiation, the insoluble product, Sb, was removed by centrifuging and decanting the excess solvent. The powder was then vigorously stirred with about 500 cubic centimeters of dry acetone to remove unreacted SbCl_3 ; the wash liquid was then removed by centrifuging followed by decanting. The metal powder was filtered onto a fritted glass filter and washed with several small batches of dry acetone. To prevent atmospheric oxidation of the Sb, care was taken to prevent the powder from drying prior to being placed under vacuum. The still-moist Sb powder was removed from the filter; dried in vacuum at 100°C to remove volatile products; heated, still in vacuum, to just below the melting point of Sb; and cooled. The purpose of the sintering operation is discussed in the next section. The weight of the sintered sample was used to calculate the Sb yield. Identification of the Sb was determined by X-ray diffraction, and the purity by chemical analysis for antimony (ref. 15).

RESULTS AND DISCUSSION

The results in table I show that antimony is deposited by electron irradiation of SbCl_3 solutions in a variety of organic liquids. For each organic liquid listed in the first column, the corresponding antimony yield is given in the second column. The yield is expressed in terms of $n \cdot G(\text{Sb})$, where n is the valence change and $G(\text{Sb})$ signifies the number of Sb atoms formed per 100 eV ($n = 3$ for the conversion of SbCl_3 to Sb). Expressing the yield in this way allows for a simple comparison of the efficiency of the process for the preparation of different metals (ref. 12). Greatest yield and highest purity of Sb were obtained from primary alcohols. Secondary alcohols gave lower yields of less pure Sb, while the nonpolar liquids (aromatic hydrocarbons) resulted in even lower yields and Sb of poor quality.

The antimony deposit was a fine black powder. The vacuum-dried powder was sensitive to atmospheric oxidation. This activity was greatest in antimony produced in the less polar liquids; frequently, deposits from aromatic hydrocarbons and esters were pyrophoric after vacuum drying. Even the vacuum-dried powder obtained from polar solvents was occasionally found to be pyrophoric. For the freshly precipitated powders, only metal deposits from tetrahydrofuran and primary and secondary alcohols produced X-ray diffraction patterns; and for these the lines for Sb were diffuse and indicated poor

crystallinity or small crystal size. Thus, black amorphous antimony was likely a major constituent in these samples and perhaps the sole constituent in those producing no pattern. Analysis of the freshly precipitated sample for antimony was not reproducible. Because of the reactivity and amorphous character of this freshly deposited metal, we chose to base our data in table I on the heat-treated (sintered) product. The sintered products give sharp X-ray diffraction lines indicating Sb metal.

As noted in the third column of table I the purity of the sintered antimony was high, 99.9+ percent antimony for methanol and 1-butanol. The analyses for antimony from toluene and ethylbenzene are also given because of our interest in these liquids as oxygen-free media for the preparation of pure metals. Aromatic hydrocarbons gave antimony of relatively low purity. Our observations reveal that the impurity in all cases is mainly carbon rather than an oxide or oxychloride of antimony. No antimony compounds were detected by X-ray diffraction; instead, a black carbonaceous residue (amorphous to X-rays) was visible after the antimony was vacuum sublimed. The residue was most prevalent in samples of low Sb assay.

We believe that the carbonaceous contaminants originate from adsorbed organic material which apparently is not removed from the fine metal powder on treatment with acetone. In the vacuum drying operation (at 100° C) this adsorbed organic material is still not removed and may in fact be decomposed or polymerized on the active metal surface. Carbonization of the organic material would then occur at the higher sintering temperature. Apparently during the preparations in which pure antimony is obtained, the acetone washing and subsequent drying is effective in removing organic adsorbates from the powder. We are hopeful that, by application of suitable extraction methods, pure antimony might possibly be obtained using aromatic hydrocarbons.

For the two organic liquids tested, with different concentrations of SbCl_3 , doubling the SbCl_3 concentration from 0.25 to 0.50 molar raised $n \cdot G(\text{Sb})$ from 2.4 to 3.6 in methanol (table I) and from 1.9 to 2.6 in tetrahydrofuran (table II). For tetrahydrofuran solutions, table II shows a steady rise in $n \cdot G(\text{Sb})$ from 0.55 to 3.7 as the SbCl_3 concentration is increased from 0.1 to 1.0 molar. Such a dependence of yield on concentration suggests that a rate-controlling step in the reaction mechanism involves the reaction of trivalent Sb with the reducing species generated by the radiation. This was not true for the aqueous copper sulfate system for which the yield of copper was essentially independent of divalent copper ion concentration (ref. 9). Of course, the reaction of copper ion as well as other metal ions with the hydrated electron is not expected to be rate controlling in water solutions. This follows from the fact that reaction rate constants of the hydrated electron with many metal ions, for example, silver (Ag^+), cadmium (Cd^{+2}), copper (Cu^{+2}), and lead (Pb^{+2}), as determined by pulse radiolysis, are greater than 10^{10} (ref. 4). Most aspects of the mechanism (e.g., the role of the solvated electron as opposed to that of the hydrogen atom) are beyond the scope of our exploratory work. It

is expedient, however, to speculate somewhat on the reason behind the dependence of yield on the chemical structure of the organic solvent. Taking into account the reaction products from the radiolysis of aliphatic alcohols, McDonell and Newton (ref. 16) claim that the principal bond rupture is at the carbinol carbon atom. Our results in table I show that high antimony yields are obtained with those alcohols (methanol, 1-butanol, and 2-propanol) which have one or more hydrogen atoms on the carbinol carbon, but poor yields result from the tertiary alcohol, 2-methyl-2-propanol, with no hydrogen on the carbinol carbon. This suggests that hydrogen atoms play a significant part in the reduction process.

Of the other organic liquids examined, only tetrahydrofuran compares favorably with primary and secondary alcohols in regard to Sb yield. As is the case with these alcohols, tetrahydrofuran also has hydrogen atoms on the carbon atom comprising the functional group. The functional group carbon atom in this cyclic ether is either of the two carbon atoms joined to the oxygen. In accord with our results for the tertiary alcohol, relatively low yields are also observed in other aliphatic organic liquids that have no hydrogen atoms on the functional group carbon. Such liquids include carboxylic acids, ketones, and esters. An anomaly is the zero yield of Sb when glycerol was used as a solvent; this may be a result of OH on adjacent carbon atoms.

CONCLUDING REMARKS

For high product yield from a radiation-induced reaction in an organic solvent, a liquid should be selected that contains one or more hydrogen atoms on the functional group carbon atom. Included in this group are primary and secondary alcohols, cyclic ethers, aldehydes, and formic acid and its esters. Simple primary alcohols have been shown to afford the greatest yield and the highest purity. However, simple primary alcohols react with the more electropositive metals. The deposition of active metals may therefore require the use of a more inert solvent such as tetrahydrofuran.

Finely divided metal powders of high surface area to volume ratio for application catalysis and powder metallurgy are best prepared from nonpolar liquids (e.g., toluene, ethylbenzene, etc.). Because of the tendency of these finely divided metal powders to adsorb organic material from solution, methods must be sought to remove such contaminants.

In addition to the deposition of metals, the radiation-induced chemical techniques presented in this report may be used for other types of inorganic preparations involving reducing conditions.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 4, 1971,
129-03.

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TABLE I. - YIELD OF ANTIMONY UPON IRRADIATION OF
ANTIMONY (III) CHLORIDE SOLUTIONS

[Electron energy, 2 MeV; SbCl_3 concentration, 0.25 molar; current, 20 μA ;
dose, 0.20 C.]

Organic solvent	Antimony yield, ^a $n \cdot G(\text{Sb})$, (valence change)(atoms Sb/100 eV)	Purity of Sb, percent
Methanol (primary alcohol)	^b 3.6	99.9+
Methanol	2.4	99.9+
1-Butanol (primary alcohol)	1.9	99.9+
Tetrahydrofuran (cyclic ether)	1.9	^c 98.6
2-Propanol (secondary alcohol)	1.6	99.0
Amyl acetate (ester)	.73	^c 94.6
Quinoline (heterocyclic base)	.40	(c)
Dibutyl phthalate (ester)	.35	-----
2-Methyl-2-propanol (tertiary alcohol)	.32	-----
Oleic acid (unsaturated acid)	.30	(c)
Toluene (aromatic hydrocarbon)	.25	^c 85
Ethylbenzene (aromatic hydrocarbon)	.25	^c 90
Acetic acid (carboxylic acid)	.20	-----
3-Heptanone (ketone)	0	-----
Glycerol (trihydroxyl alcohol)	0	-----

^aProduct after sintering shown to be Sb metal by X-ray diffraction.

^b SbCl_3 concentration, 0.50 molar.

^cPortions of the samples were sublimed, and carbonaceous residues were observed.

TABLE II. - EFFECT OF ANTIMONY (III) CHLORIDE
CONCENTRATION ON ANTIMONY YIELD

[Tetrahydrofuran solutions; electron energy, 2 MeV;
current, 20 μA ; dose, 0.20 C.]

SbCl_3 concentration, moles/1000 cm^3	Antimony yield, $n \cdot G(\text{Sb})$, (valence change)(atoms Sb/100 eV)
0.1	0.55
.2	1.3
.25	1.9
.50	2.6
1.0	3.7

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